FORMULA: Hg

M.W.: 200.59

MERCURY

METHOD: 6009
ISSUED: 5/15/89

OSHA: 0.05 mg/m^3 (skin)
NIOSH: 0.05 mg/m^3 (skin) [1]
ACGIH: 0.05 mg/m^3

PROPERTIES: liquid; d 13.55 g/mL @ 20 °C; BP 356 °C; MP -39 °C; VP 0.16 Pa (0.0012 mm Hg; 13.2 mg/m^3) @ 20 °C

SYNONYMS: quicksilver; CAS# 7439-97-6.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Hydrar in single section, 200 mg)

FLOW RATE: 0.15 to 0.25 L/min

VOL-MIN: 2 L @ 0.05 mg/m^3
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 30 days @ 25 °C [2]

FIELD BLANKS: 10% of samples
MEDIA BLANKS: at least 3 per set

ACCURACY

RANGE STUDIED: 0.002 to 0.8 mg/m^3 [3]
(10-L samples)

BIAS: not significant [2,3]

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, COLD VAPOR

ANALYTE: elemental mercury

DESORPTION: conc. HNO_3/HCl @ 25 °C, dilute to 50 mL

WAVELENGTH: 253.7 nm

CALIBRATION: standard solutions of Hg^{++} in 1% HNO_3

RANGE: 0.1 to 1.2 µg per sample

ESTIMATED LOD: 0.03 µg per sample

PRECISION (s_r): 0.042 @ 0.9 to 3 µg per sample [4]

APPLICABILITY: The working range is 0.01 to 0.5 mg/m^3 for a 10-L air sample. The sorbent material irreversibly collects elemental mercury. A prefilter can be used to exclude particulate mercury species from the sample. The prefilter can be analyzed by similar methodology. The method has been used in numerous field surveys [4].

INTERFERENCES: Inorganic and organic mercury compounds may cause a positive interference. Oxidizing gases, including chlorine, do not interfere.

OTHER METHODS: This replaces method 6000 and its predecessors, which required a specialized desorption apparatus [5,6,7]. This method is based on the method of Rathje and Marcero [8] and is similar to the OSHA method ID 145H [3].

REAGENTS:

1. Water, organics-free, deionized.
2. Hydrochloric acid (HCl), conc.
3. Nitric acid (HNO_3), conc.
4. Mercuric oxide, reagent grade, dry.
5. Calibration stock solution, Hg++, 1000 µg/mL. Commercially available or dissolve 1.0798 g of dry mercuric oxide (HgO) in 50 mL of 1:1 hydrochloricacid, then dilute to 1 L with deionized water.
6. Intermediate mercury standard, 1 µg/mL. Place 0.1 mL 1000 µg/mL stock into a 100 mL volumetric containing 10 mL deionized water and 1 mL hydrochloric acid. Dilute to volume with deionized water. Prepare fresh daily.
7. Stannous chloride, reagent grade, 10% in 1:1 HCl. Dissolve 20 g stannous chloride in 100 mL conc. HCl. Slowly add this solution to 100 mL deionized water and mix well. Prepare fresh daily.
8. Nitric acid, 1% (w/v).

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame sealed ends with plastic caps, containing one section of 200 mg Hydrar held in place by glass wool plugs (commercially available from SKC, Inc., Cat. #226-17-1).
   NOTE: A 37-mm, cellulose ester membrane filter in a cassette preceding the Hydrar may be used if particulate mercury isto be determined separately.
2. Personal sampling pump, 0.15 to 0.25 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with cold vapor generation system (see Appendix) or cold vapor mercury analysis system.*
4. Strip chart recorder.
5. Flasks, volumetric, 50-mL, and 100-mL.
6. Pipet, 5-mL, 20-mL, others as needed.
7. Micropipet, 10- to 1000-µL.
8. Bottles, biological oxygen demand (BOD), 300-mL.

*See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Mercury is readily absorbed by inhalation and intact skin. Operate the mercury system in a hood, or bubble vented mercury through a mercury scrubber.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately prior to sampling. Attach sampler to pump with flexible tubing.
3. Sample at an accurately known flow rate of 0.15 to 0.25 L/min for a sample size between 2 and 100 L.
   NOTE: Include a minimum of three unopened sampling tubes from the same lot as the samples for use as media blanks.
4. Cap sampler and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the Hydrar sorbent and the front glass wool plug from each sampler in separate 50-mL volumetric flasks.
6. Add 2.5 mL conc. HNO_3 followed by 2.5 mL conc. HCl.
   NOTE: The mercury must be in the oxidized state to avoid loss. For this reason, the nitric acid must be added first.
7. Allow the sample to stand for 1 hour or until the black Hydrar sorbent is dissolved. The solution will turn dark brown and may contain undissolved material.
8. Carefully dilute to 50 mL with deionized water. (Final solution is blue to blue-green).
9. Using a volumetric pipet, transfer 20 mL of the sample to a BOD bottle containing 80 mL of deionized water. If the amount of mercury in the sample is expected to exceed the standards a smaller aliquot may be taken, and the volume of acid adjusted accordingly. The final volume in the BOD bottle must be 100 mL. To prevent possible loss of mercury during transfer, place the pipet tip below the surface of the liquid in the BOD bottle.

CALIBRATION AND QUALITY CONTROL:

10. Prepare a minimum of two series of working standards covering the range 0.01 to 0.5 µg Hg per aliquot by adding known amounts of the intermediate standard to BOD bottles containing enough 1% nitric acid to bring the final volume to 100 mL.
11. Analyze the working standards together with the samples and blanks (steps 13 through 16). Analyze full set of standards at the beginning of the run, and a second set at the end of the run. Additional standards may be run intermediately during the analysis to confirm instrument response.
12. Prepare calibration graph (peak height from the recorder vs. solution concentration, µg/sample).

MEASUREMENT:

13. Zero the spectrophotometer by removing the bubbler from the BOD bottle, allowing the baseline on the recorder to stabilize.
14. Place the bubbler in a BOD bottle containing 0.5 µg mercury in 100 mL 1% nitric acid. Adjust the spectrophotometer so that it will give a 75% to full-scale deflection of the recorder.
15. Vent the mercury vapor from the system.
16. Analyze standards, samples and blanks (including media blanks).
    a. Remove the bubbler from the BOD bottle.
    b. Rinse the bubbler with deionized water.
    c. Allow the recorder tracing to establish a stable baseline.
    d. Remove the stopper from the BOD bottle containing the next sample to be analyzed. Gently swirl the BOD bottle.
    e. Quickly add 5 mL 10% stannous chloride solution.
    f. Quickly place the bubbler into the BOD bottle.
    g. Allow the spectrophotometer to attain maximum absorbance.
    h. Vent the mercury vapor from the system.
    i. Rinse the bubbler using deionized water.
    i. Place the bubbler into an empty BOD bottle. Continue venting the mercury until a stable baseline is obtained.
    j. Close the mercury vent.

CALCULATIONS:

17. Calculate the amount of mercury in the sample aliquot (W,µg) from the calibration graph.
18. Calculate the concentration C (mg/m^3), of mercury in the air volume sampled, V (L):

$$C = [W \bullet (Vs/Va) - B]/V$$

Where:
Vs = original sample volume (step 8; normally 50 mL)
Va = aliquot volume (step 9; normally 20 mL)
B = average amount of mercury present in the media blanks

EVALUATION OF METHOD:

Rathje and Marcero originally used Hopcalite (MSA, Inc.) as the sorbent material [8]. Later, Hopcalite was shown superior to other methods for the determination of mercury vapor [9]. Atmospheres of mercury vapor for the study were dynamically generated in the range 0.05 to 0.2 mg/m^3 and an adsorbent tube loading of 1 to 7 µg was used. The Hydrar material used in the present method is similar to Hopcalite. No significant difference in the laboratory analysis of mercury collected on the two sorbent materials was observed [10]. OSHA also validated a method for mercury using Hydrar [3]. An average 99% recovery, with $s_r = 0.042$, was seen for 18 samples with known amounts (0.9 to 3 µg) of mercury added (as $Hg(NO_3)_2$) [11]. No change in recovery was seen for samples stored up to 3 weeks at room temperature or up to 3 months at −15 °C; longer storage times were not investigated [11].

REFERENCES:

[1] NIOSH Testimony, OSHA Proposed Rules on Air Contaminants, Docket #H-020, August 1, 1988.

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[5] NIOSH Manual of Analytical Methods, 3rd. ed., Method 6000. (1984).
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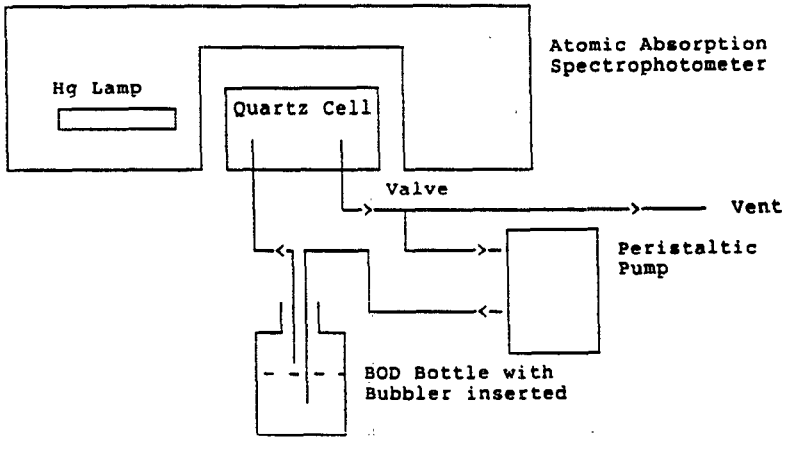
[9] McCammon, C. S., Edwards, S. L., Hull, R. D., Woodfin, W. J., A comparison of four personal sampling methods for the determination of mercury vapor, Am. Ind. Hyg. Assoc. J., 41:528-531 (1980).
[10] Internal Methods Development Research, Data Chem, Inc., Salt Lake City, Utah (1982).
[11] Eller, P.M., NIOSH, unpublished data (1987-88).

METHOD WRITTEN BY: Keith R. Nicholson and Michael R. Steele, Data Chem, Inc., Salt Lake City, Utah. under NIOSH contract No. 200-87-2533.

APPENDIX: Cold Vapor Mercury Analysis System



1. The valve should direct the vented vapors to a hood or to a mercury scrubber system.
2. When the valve is opened to "Vent" the peristaltic pump should draw room air. Place a Hydrar tube in the air intake to eliminate any mercury that may be present.
3. Adjust the peristaltic pump to a flow which will create a steady stream of bubbles in the BOD bottle, but not so great that solution droplets enter the tubing to the quartz cell.
4. If water vapor condenses in the quartz cell, heat the cell slightly above room temperature by wrapping it with a heating coil and attaching a variable transformer.
5. The bubbler consists of a glass tube with a bulb at the bottom, slightly above the bottom of the BOD bottle. The bulb contains several perforations to allow air to escape into the solution (in a stream of small bubbles). A second tube is provided to allow the exit of the vapor. The open end of the second tube is well above the surface of the liquid in the bottle. The two tubes are fixed into a stoppering device (preferably ground glass) which fits into the top of the bottle. A coarse glass frit can be used in place of the bulb on the first tube. However, it is more difficult to prevent contamination when a frit is used.
6. Replace the flexible tubing (Tygon or equivalent) used to connect the bubbler, cell, and pump periodically to prevent contamination due to adsorption of mercury.